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EVALUATION OF COMPATIBLE PROCESSING ROUTES USING THERMAL TREATMENT FOR UPGRADING OF MOPA MURO AND OBAN MASSIF MANGANESE DEPOSITS

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ABSTRACT

The present study deals with evaluation and compatibility of processing routes using thermal treatment for upgrade of mopa muro and oban Massif manganese ore deposits**.** The study samples are characterized by XRD, XRF and SEM analysis. The results of SEM analysis show the micro-cracks in the thermally treated manganese sample, Mineralogical investigation shows that in the Mopa Muro manganese ore, most of the Manganese occurs in the silicate managenese mineral as in Almandine $(Fe^{2+})_3Al_2(SiO_4)_3$, Spessartine$(Mn^{2+})_3Al_2(SiO_4)_3$, Clinochlore (Al-Fe-SiO_2-OH), Geothite FeO(OH),while the Oban Massif is rich in, Pyrolusite MnO_2, Clinochlore (Al-Fe-SiO_2-OH), and Spessartine$(Mn^{2+})_3Al_2(SiO_4)_3$. The mineralogy of the two deposits also revealed that there is a Free Silica (Quartz) in abundant. The low content of sulphur and phosphorus is however within the requirement of the metallurgical grade manganese ore, while 44.08% and 42.07% of manganese (Mn) obtained for Mopa Muro and Oban Massif manganese ores respectively after all analysis indicate apparent inability of the ores meet the requirement of metallurgical grade manganese with values less than 66% recommended specification using thermal treatment.

Keywords: Thermal Treatment, mineralogy analysis, Manganese Ore.

INTRODUCTION

Manganese is one of the most widely used and versatile chemical elements in the world which is found naturally in the form of mineral deposits in varieties of composition associated with metallic, non-metallic and/or volatile or extraneous materials [1]. It plays a vital role in various industrial applications. It is primarily used in the production of steel, where it improves the strength, durability, and resistance to wear and tear of the final product. However, the availability of high-grade manganese ores has been declining rapidly over the years, necessitating the development of alternative methods for the extraction and upgrading of lower-grade manganese deposits. The beneficiation of a mineral from any of such depositions require the engagement of one or several enrichment technique(s) deigned at obtaining suitable

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products dictated by end users [2]; as each manganese deposit is considered unique vis-à-vis its concentrate and gangue constituents [3]. Moreover, specification of the various sectors using manganese as primary or complementary raw material is not uniform.

The backbone of any national techno-economic development, including Nigeria is the sustainability of iron and steel production. The iron and steel industry produces a range of products and consumes numerous amounts of input elements. The steel sector in the developed economies is the highest employer of labour of the entire economic sector with its multiplier effect. Because of their importance, the steel company in the Republic of South Korea made a bold inscription on its entrance: "A nation that controls iron and steel controls the world economically" – Pohang Steel Company Ltd. [4]. However, several obnoxious political policies, technical, logistical and managerial challenges, forced the iron and steel companies owned by individual to fold up in Nigeria [5]. Due to lack of sustainable raw materials which are mills – roll up type that dependent on billets through integrated mills. Raw materials such as iron ore, manganese ore, coal, and limestone are in abundant in Nigeria which are required for steel development. Between "1975 – 1980" Nigeria constructed two integrated iron and steel plants located at Ajaokuta (ASC) and Aladja (DSC) and the three rolling mills company at Oshogbo, Jos and Kastina [6]. With continuous mass importation of iron and steel products into Nigeria without internal production in sustainable basis and good time, the following are bound to happen; more buildings will collapse, more graduates will remain unemployed, more brain drain will take place, the value of the national currency will diminish more and more as well as trading options for the nation will remain closed off. Steel consumption depends on the growth of the economy, Governments investment in infrastructure, transportation, and building of new factories the beneficiation of manganese ores may involve any or a combination of physical and extractive metallurgy techniques in the enrichment of the crude ores [7]. [8]. The processing of manganese ores is similar to that of iron ores which are crushed and screened. The ores coarse product generally smelted, while the fine product are used as feed for chemical and/or electrolytic processing [3]. In case of fine manganese ores, the upgrading usually involve sink-float, jigging, tabling, flotation and high-intensity magnetic separation, whereas flotation and roasting, and chemical separation process such as leaching are for beneficiation of lower grade and more refractory resources]3].

The physical technique(s) is mostly in order of, comminution, sizing and concentration processes [7], [2]. Whereas the extractive techniques involve chemical transformation processes that go beyond comminution and concentration [8] to extract a product in the form of manganese metal or alloy(s). At times, intermediate upgrading may be required to make the mineral amenable to

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concentration or extraction processes. These approaches are applicable to all grades and types of manganese ores depending on whether they are liberated after milling or not [9].

Manganese numerous applications affect a lot of our daily lives as it is used in food, fertilizer, fungicides, frits, flux, fragrance, flavours, ferrites, fluorescent tubes, fine chemicals, ferric leaching, ferroalloys etc [9]; [3]; [1]; [10]. Manganese serves as an oxidant, deoxidant, colourant, bleach, insecticide, bactericide, algicide, lubricant, nutrient, catalyst, drier, scavenger, etc (Evans, 2012). Hence, the upgrade and improvement of the available ore in Nigeria becomes necessary. Thus the evaluation of compatible processing methods for possible improvement of Mopa Muro (Kogi State) and Oban Massif (Cross river State) manganese ore deposits is a timely positive effort and houses [11]. The two significant manganese deposits in Nigeria, Mopa Muro and Oban Massif, present significant opportunities for manganese production. However, these deposits consist of lower-grade manganese ores, which require upgrading to meet the desired quality for steel production. Thermal treatment processes have shown promise in upgrading such ores efficiently and economically, making it an attractive option for the processing of Mopa Muro and Oban Massif manganese deposits. Therefore, the objective of this paper is to evaluate the compatibility of processing routes using thermal treatment for upgrading of mopa muro and oban Massif manganese deposits**.**

MATERIALS AND METHODS

Sample Preparation

Exactly 50kg of manganese sample each collected from Mopa Muro and Oban Massif study areas were used for the research work, a representative sample for the total analyses was taken by crushing the 50kg in Herzog laboratory jaw crusher. The product was screened to 100% of ±75µm with Herzog Vibrating cup Mill. The +75µm was retained and the -75 µm further screen until homogeneity was achieved. The product was screened for quartering and the two adjacent sample was packed, bagged and ready for analyses while the other remaining two adjacent were packed, bagged and save for further use. The -75µm pass (undersize) materials from each deposits site was divided into two and 25g of samples were used for the XRF and XRD characterization. The coarser materials (i.e. > 80 mm) was used in other analyses like beneficiation [12].

Preparation Of Reagents

I **Preparation of 5% Sodium Sulphide**: 5 g of the reagent was weighed into 100 ml flask and diluted with distilled water to the mark. Assay: Density-1.86g/cm^3, Molecular weight- 78.0472g/mol.

ii **Preparation of 6% Sodium hexametaphosphate**: 6 g of the reagent was weighed into 100 ml flask, and was

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diluted with distilled water to the mark. Assay: Density-2.48g/cm^3, Molecular weight- 611.77g/mol.

Characterization Studies

Investigation of mineralogy, size of assay on Mopa Muro and Oban Massif manganese ores samples. The sample used in this work was obtained from Kogi and cross rivers state deposit of Manganese ore Mining located in Nigeria. Identification of the types of minerals in the sample, uses X-ray diffraction (XRD) analyzer (model PW1800) with a copper tube was used. The XRD analysis showed that the main minerals of the sample included contained three minerals viz: Almandine $(Fe^{2+})_3$ $Al_2(SiO_4)_3$, Manganosite(MnO), and Quartz (SiO_2), Beryl (Be_3SiO_4 $(OH)_2.H_2O$), Geothite FeO(OH), Pyrolusite MnO_2, Clinochlore (Al-Fe-SiO_2-OH).

SEM and X- ray fluorescence spectroscopy (XRF) analyses were carried out to identify the Minerals present in the sample, and the results obtained were shown in Table 2. The results obtained indicated that SiO_2, Al_2O_3, MnO, BaO, Fe_2O_3, TiO_2, NiO, Cr_2O_3, V_2O_5, Ta_2O_5, SO_3, CaO, Nb_2O_5, CuO, P_2O_5, Co_3O_4 were present at various percentage compositions.

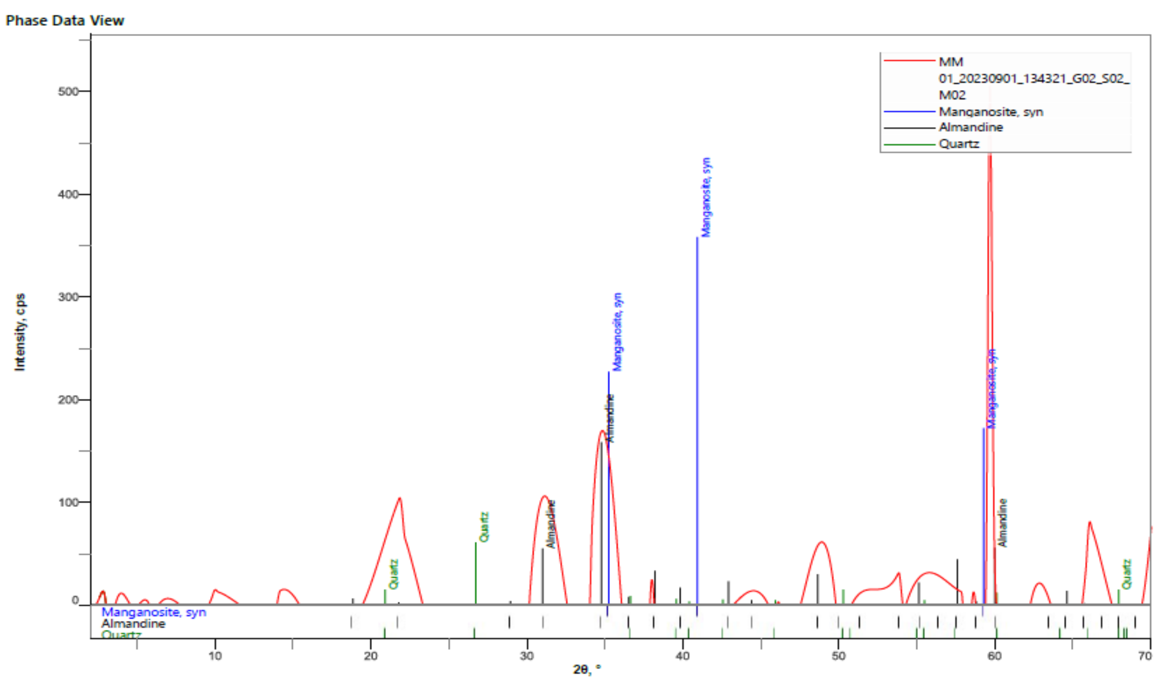

Figure 2.1: Diffractogram showing the Mineral phase distribution of Mopa Moro Manganese Ore

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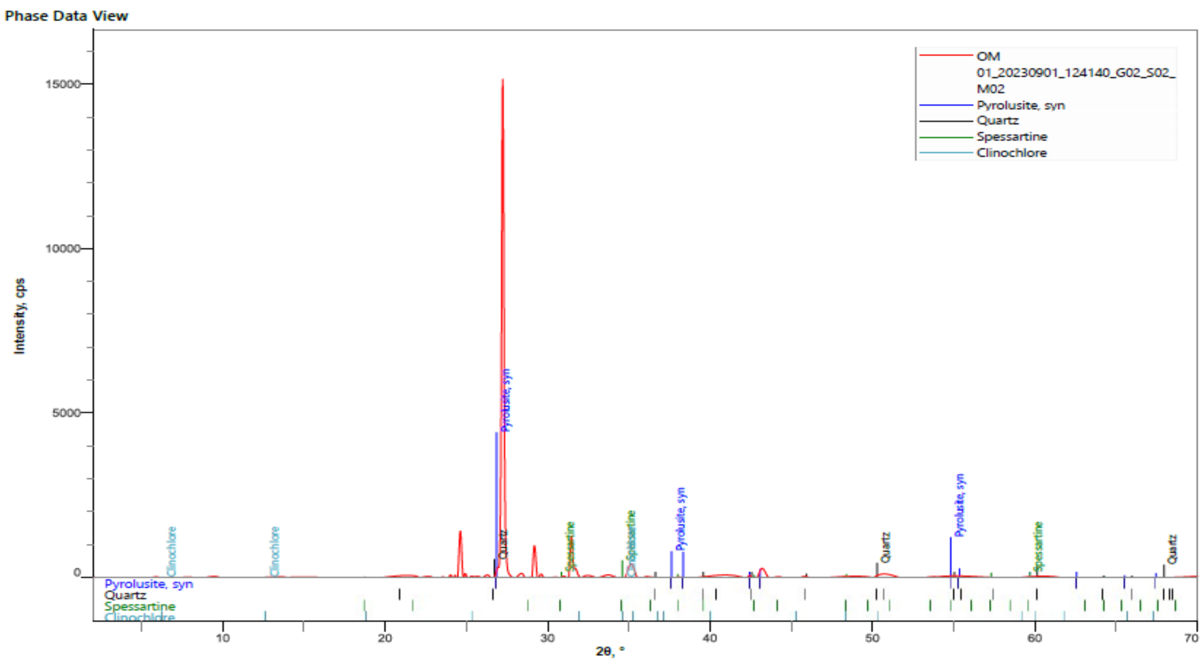

Figure 2.2: Diffractogram showing the Mineral phase distribution of Oban Massif Manganese Ore

RESULTS AND DISCUSSION

Mineralogical Analysis

Table .3.1a and 3.1b, Figure 3.1a and 3.1b show the qualitative mineralogical composition and diffractogram peaks of the Mopa Muro and Oban Massif manganese ore generated by XRD. From Table 3.1a, sample MM-01 contained three minerals viz: Almandine$(Fe^{2+})_3Al_2(SiO_4)_3$, Manganosite(MnO), and Quartz (SiO_2), with manganosite having 53% as highest value, MM-02 contained four minerals viz: Almandine$(Fe^{2+})_3Al_2(SiO_4)_3$, Manganosite(MnO), Clinochlore (Al-Fe-SiO_2-OH) and Quartz (SiO_2), with Almandine having 48% as highest value. MM-03 contained five minerals viz: Beryl (Be_3SiO_4 (OH) 2.H_2O), Manganosite (MnO), Clinochlore (Al-Fe-SiO_2-OH), Quartz (SiO_2) and Spessartine $(Mn^{2+})_3Al_2(SiO_4)_3$, with 63% Spessartine as highest value. MM-07 contained six minerals viz: Beryl (Be_3SiO_4 (OH) $_{2.H2O}$), Geothite FeO(OH), Pyrolusite MnO_2, Clinochlore (Al-Fe-SiO_2-OH),

Table 3.1a Mineralogical composition of Mopa Muro manganese ore

Qualitative Composition		**Quantitative Composition**										
Mineral	**Chemical Formula**	**MM-01**	**MM-02**	**MM-03**	**MM-04**	**MM-05**	**MM-06**	**MM-07**	**MM-08**	**MM-09**	**MM-10**	**Occurrence**
Almandine	**$(Fe^{2+})_3Al_2(SiO_4)_3$**	36	48	-	39	40	55	-	42	22	25	8
Beryl	**$Be_3SiO_4(OH)_2.H_2O$**	-	-	-	-	-	-	7.0	-	-	-	1
Goethite	**FeO(OH)**	-	-	8.1	0.05	15.6	-	4.8	11.8	22	-	6
Pyrolusite	**MnO_2**	-	-	13.5	-	-	4.2	10.8	-	-	24.9	4
Clinochlore	**Al-Fe-SiO_2-OH**	-	2	10.4	22.9	-	-	0.09	2	-	0.5	6
Manganosite	**MnO**	53	39	-	-	-	-	-	-	-	-	2
Quartz	**SiO_2**	11	11	5.2	2	5.2	7.5	62	2	15	49.5	10
Spessartine	**$(Mn^{2+})_3Al_2(SiO_4)_3$**	-	-	63	36	39	34	16	42	42	-	7
	Occurrence	**3**	**4**	**5**	**5**	**4**	**4**	**6**	**5**	**4**	**4**	**44**
	Total%	**100**	**100**	**100**	**100**	**100**	**100**	**100**	**100**	**100**	**100**	**-**

KEY; XRD= X-ray Diffractometer

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Table 3.1b Mineralogical composition of Oban Massif manganese ore

Qualitative Composition		**Quantitative Composition**										
Mineral	**Chemical Formula**	**OM-01**	**OM-02**	**OM-03**	**OM-04**	**OM-05**	**OM-06**	**OM-07**	**OM-08**	**OM-09**	**OM-10**	**Occurrence**
Almandine	$(Fe^{2+})_3Al_2(SiO_4)_3$	-	12	-	-	38	-	-	-	10.0	40	4
Goethite	$FeO(OH)$	-	-	19.4	19.1	-	1	0.5	7	-	-	5
Pyrolusite	MnO_2	54	24	30	27	19.5	30.2	48	29.7	27.9	-	9
Clinochlore	$Al\text{-}Fe\text{-}SiO_2\text{-}OH$	0.05	4	8.3		5	0.07	0.3	12.6	0.16	12	9
Quartz	SiO_2	39	39	42	18.7	31	56.6	33	44.5	52.8	13	10
Spessartine	$(Mn^{2+})_3Al_2(SiO_4)_3$	7.2	20	-	35.0	6	12.1	18	6.5	9.1	-	8
Manganosite	MnO	-	-	-	-	-	-	-	-	-	35	1
	Occurrence	**4**	**5**	**4**	**4**	**5**	**5**	**5**	**5**	**5**	**4**	**46**
	Total%	**100**	**100**	**100**	**100**	**100**	**100**	**100**	**100**	**100**	**100**	**-**

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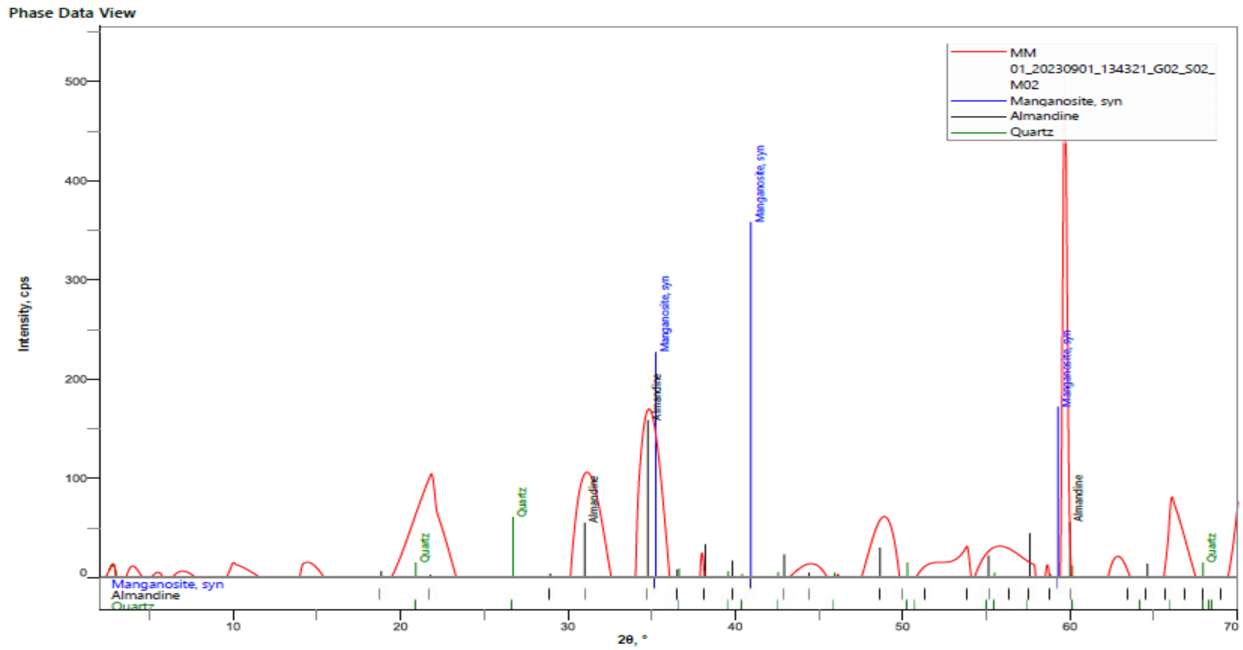

Figure 3. 1a: Diffractogram showing the Mineral phase distribution of Mopa Moro Manganese Ore

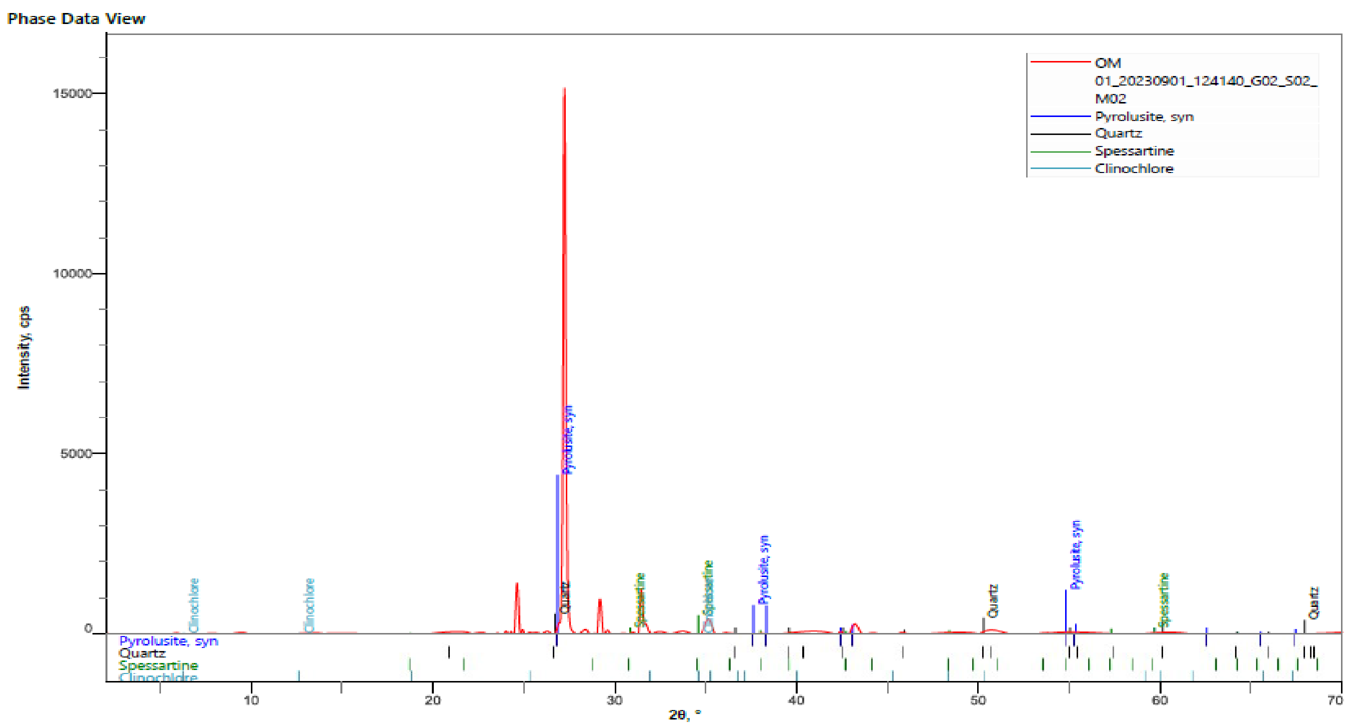

Figure 3.1b: Diffractogram showing the Mineral phase distribution of Oban Massif Manganese Ore

SEM- Morphology Mineral Phases

Plates 3.2a and 3.2b are the SEM photomicrographs of the Mopa Muro and Oban Massif manganese ores taken at different magnifications and particle sizes. From these micrographs, it can be seen that a wide range of phases could be identified which were not detected by XRD. The phases are at the magnification of x1000 (Mag: x1000). Plate 3.2 as automatically indicated photomicrograph has a particle size of 33.1 **µm** while Plate 3.2b has a particle size of 86.3 **µm** at analyzing particle range size of 80 **µm** respectively. The morphology expression further show clearly that the mineral phases are finely disseminated and intermittently inter-grown with each other, which implies that very fine grinding is necessary as indicated in the degree of liberation. Also, the Plates show back scattered election image (BEI) which pointed to the fact that the ore is highly porous and the porosity is a contributing factor in separation techniques**.**

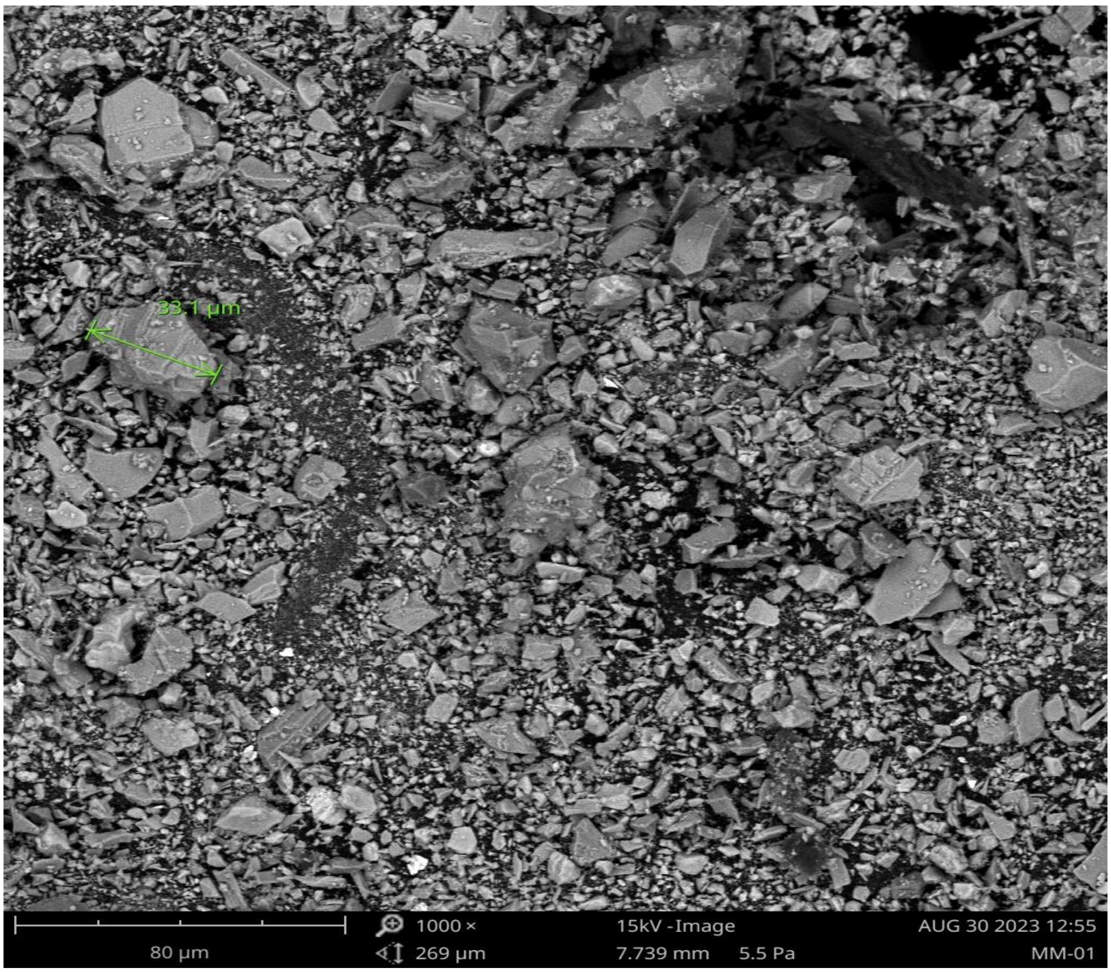

Plate 3.2a: SEM image showing the morphology patterns of sample MM – 01

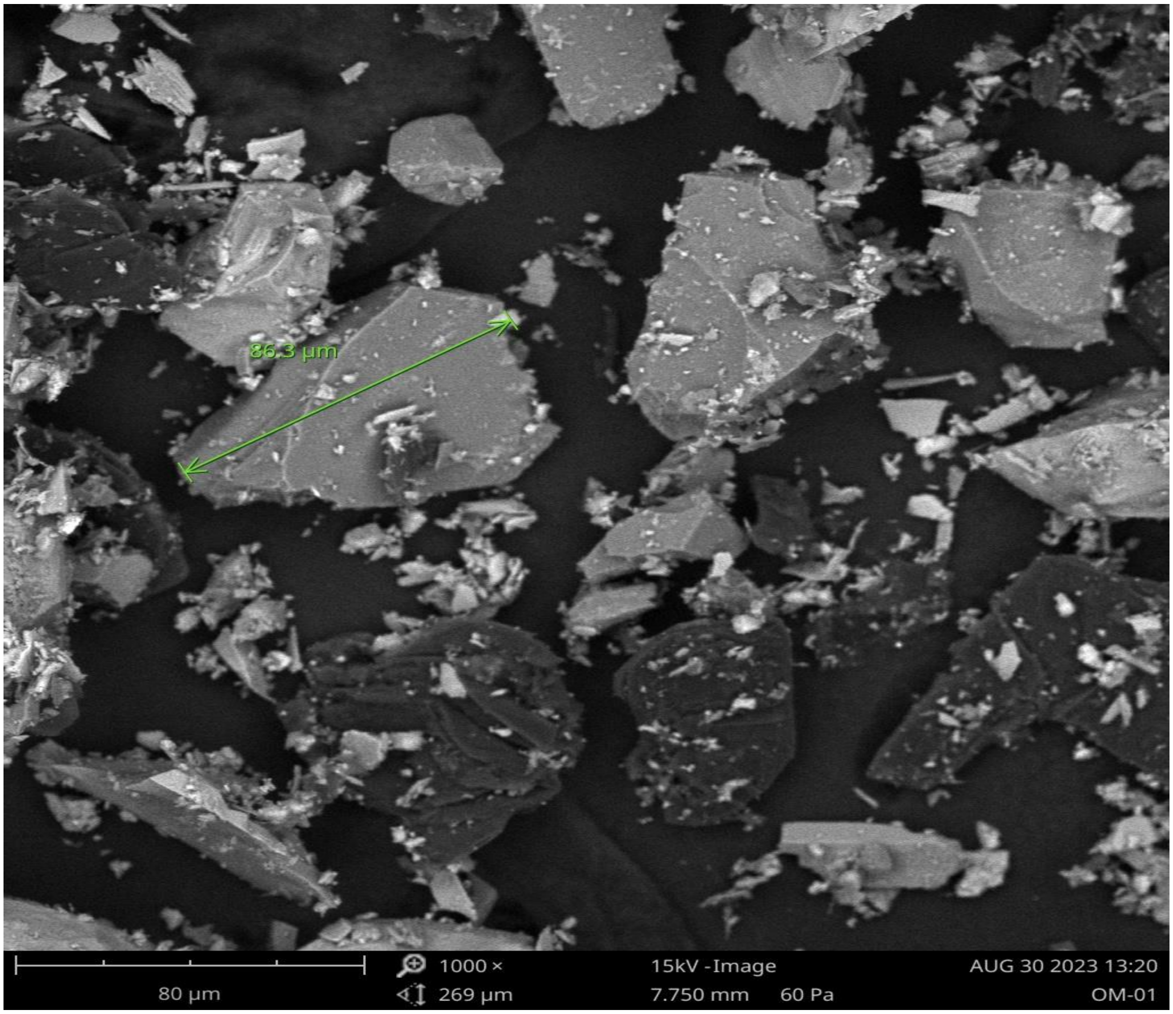

Plate 3.2b: SEM image showing the morphology patterns of sample OM – 01

Elemental Composition

The study of elemental constituents of the samples were obtained using X –ray fluorescence equipment on total of twenty four (24) samples, twelve samples each from both deposits. The following results presented in Tables 3.3a and 3.3b were generated.

Tables 3.3a and 3.3b show the chemical analysis of the Mopa Muro and Oban massif Manganese ores.

From the tables, substantial amount of Iron, Aluminum, Titanium and Silica associated with the manganese ore are obvious and constitute major elements. The percentage of the Silica represents both free Silica which occurs as quartz and chemically combined silica which occurs either with manganese or Alumina and Iron. The elements Calcium, Potassium, Phosphorous, Niobium, Sulphur and Titanium occur as minor elements, Cobalt, Copper, Zinc, Vanadium, Tantalum and Chromium as trace elements (see Appendix. 1 to 10).

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Based on the percentage concentration of manganese obtained in this chemical analysis viz: manganese (36.62%), silica (34.86%) and Alumina (11.17%) from Mopa Muro Manganese ore and manganese (32.89%), silica (32.17%) and Alumina (11.95%) from Oban Massif, the concentration of manganese in both ore are considered low grade manganese ores and does not meet the specification of a metallurgical grade manganese Ore (Table 3.3b). However, other minor and trace parameters are within the acceptable range. Based on the results of the natural state of manganese ore from Mopa Muro and Oban Massif, the ores must undergo thorough beneficiation process before it could be used for ferromanganese production.

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Table 3.3a: XRF Results of Mopa- Muro Manganese ore Samples

Sample ID	% COMPOSITION															
	SiO_2	Al_2O_3	BaO	MnO	Fe_2O_3	TiO_2	NiO	Cr_2O_3	V_2O_5	Ta_2O_5	SO_3	CaO	Nb_2O_5	CuO	P_2O_5	Co_3O_4
MM 01	29.17	7.27	0.29	41.61	11.52	0.78	0.43	0.01	0.05	0.01	0.31	6.63	0.28	0.08	1.15	-
MM 02	37.30	7.08	0.39	32.69	14.14	1.31	0.47	0.004	0.08	0.04	0.25	4.52	0.14	0.07	1.30	-
MM 03	43.23	9.70	0.27	25.77	12.77	0.99	0.03	0.02	0.14	0.04	0.35	5.53	0.17	0.06	0.83	-
MM 04	39.53	7.51	0.87	31.85	12.29	1.05	0.44	0.01	0.09	0.03	1.77	3.31	-	0.09	0.86	-
MM 05	26.76	10.51	0.38	41.69	13.34	1.25	0.03	-	0.11	0.07	0.22	3.37	0.05	0.10	0.10	-
MM 06	28.01	10.63	0.32	40.77	15.20	1.15	0.02	0.01	0.13	0.02	0.32	6.04	0.39	0.06	0.11	-
MM 07	29.10	13.10	0.22	37.61	14.35	0.80	0.06	0.03	0.06	0.01	0.15	7.36	0.11	0.08	1.71	0.01
MM 08	27.22	17.20	0.47	39.10	14.42	0.79	0.38	0.01	0.06	0.01	0.55	4.36	0.12	0.08	0.93	-
MM 09	35.93	16.59	0.23	29.15	15.49	1.00	0.01	0.03	0.13	0.02	0.29	6.14	0.04	0.04	1.39	0.02
MM 10	25.27	12.11	0.70	45.92	11.06	1.69	0.02	0.02	0.12	0.07	0.19	3.38	0.11	0.09	0.32	-
AVERAGE	**34.86**	**16.17**	**0.51**	**36.62**	**18.49**	**2.08**	**0.19**	**0.09**	**0.10**	**0.03**	**0.44**	**5.06**	**0.16**	**0.12**	**0.87**	**0.02**

KEY; XRF = X-Ray Flourescence

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Table 3.3b: XRF Results of Oban- Massif Manganese Samples

Sample ID	% COMPOSITION															
	SiO_2	BaO	Al_2O_3	MnO	Fe_2O_3	TiO_2	CuO	Nb_2O_5	ZnO	SO_3	K_2O	Co_3O_4	V_2O_5	Cr_2O_3	P_2O_5	Ta_2O_5
OM 01	41.75	0.21	9.93	27.46	12.65	1.96	0.09	0.02	0.03	0.34	0.002	-	0.11	0.02	-	0.01
OM 02	42.43	0.30	11.91	30.56	7.77	0.58	0.02	0.34	0.02	0.13	0.07	-	0.07	0.01	-	0.02
OM 03	42.47	0.05	16.15	26.01	10.30	1.64	0.03	0.28	0.01	0.50	-	-	0.10	0.05	0.01	0.04
OM 04	22.50	0.25	15.16	42.16	14.94	1.48	0.05	0.38	0.02	0.65	0.17	-	0.09	0.03	0.20	0.10
OM 05	21.52	0.26	15.97	40.47	12.92	1.20	0.07	0.25	0.01	0.20	0.01	-	0.12	0.02	0.18	0.04
OM 06	32.92	0.07	10.76	31.90	14.37	2.04	0.07	0.05	0.01	0.56	0.18	-	0.07	0.06	0.12	0.04
OM 07	45.77	0.10	6.42	22.50	13.11	1.49	0.04	0.02	0.03	0.69	0.73	0.01	0.11	0.03	0.22	0.04
OM 08	33.22	0.02	7.18	35.71	13.08	1.55	0.06	0.24	0.01	0.59	0.04	-	0.10	0.05	-	0.04
OM 09	45.66	0.06	10.75	18.74	13.01	1.96	0.11	0.05	0.02	0.34	-	-	0.07	0.02	0.16	0.04
OM 10	23.47	0.11	15.31	43.37	30.09	0.71	0.05	0.55	0.02	1.03	0.27	0.02	0.10	0.04	-	0.04

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AVERAGE	**32.17**	**0.14**	**21.95**	**31.89**	**14.22**	**1.98**	**0.09**	**0.22**	**0.01**	**0.50**	**0.15**	**0.001**	**0.09**	**0.03**	**0.20**	**0.04**	

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CONCLUSION

The aim of this work was to development a process route for upgrading of Mopa Muro and Oban Massif manganese ore deposits to ferromanganese feed grade, conducted thoroughly in two phases. The first phase involved carrying out mineralogical analyses, chemical analyses, and morphological studies to confirm the mineralogical constituents, elemental compositions of the ore and the morphological structure of the samples used for the study. Mineralogical investigation shows that in the Mopa Muro manganese ore, most of the Manganese occurs in the silicate manganese mineral as in Almandine $(Fe^{2+})_3Al_2(SiO_4)_3$, Spessartine$(Mn^{2+})_3Al_2(SiO_4)_3$, Clinochlore (Al-Fe-SiO_2-OH), Geothite $FeO(OH)$,while the Oban Massif is rich in, Pyrolusite MnO_2, Clinochlore (Al-Fe-SiO_2-OH), and Spessartine$(Mn^{2+})_3Al_2(SiO_4)_3$. The mineralogy of the two deposits also revealed that there is a Free Silica (Quartz) in abundant.

SEM analysis showed micro-cracks in the thermally treated manganese sample, the Mopa Muro and Oban Massif manganese ores have been successfully beneficiated using difference separation techniques with enhancement of the grade of Mopa Muro by 7.46% and Oban Massif by 5.55% respectively. The Mopa Muro and Oban Massif manganese ores from the result after all analyses indicated the values of 44.08% Mn and 42.07%Mn. Apparently, these values shows that manganese ores obtained using this processing route does not meet the requirement of metallurgical grade manganese with values less than 66% recommended specification. Therefore, the low content of sulphur and phosphorus is however within the requirement of the metallurgical grade manganese ore.

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Conflicts of Interest: The authors declare no conflict of interest.

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